Fundamental Study of Selective Separation of Soft Metals by Microcapsules Enclosed with Extractants

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論 文 内 容 要 旨

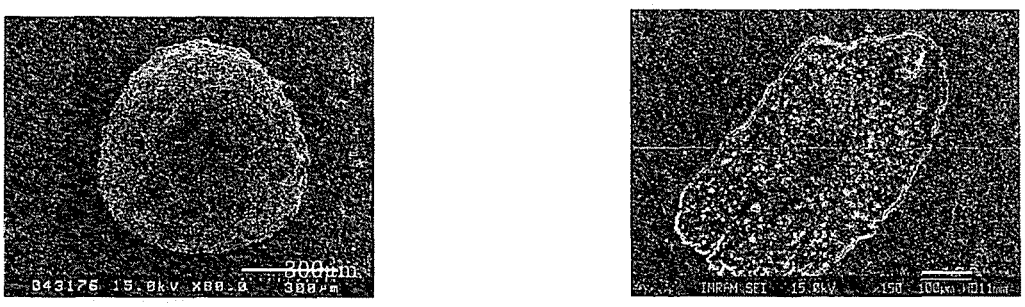
In the past few years there has been a great deal of researches on partitioning-transmutation of high level radioactive liquid waste (HLLW) generated in nuclear fuel reprocessing. So far, most of the developed partitioning schemes have merely targeted the separation-transmutation of transuraniums and in fewer cases ^{99}Tc, ^{137}Cs and ^{90} Sr. But the so called "Four group process", of JAERI proposed the separation of PGMs in addition to above-mentioned radiotoxic elements. It is believed that if in the future, the partitioning of HLLW becomes commercial, benefit of separation of precious PGMs can to an extent balance the total investments of the partitioning process.

Among the three abundant PGMs in HLLW (*i.e.* Ru, Pd, Rh), the amount of ruthenium is the highest, but industrial demand for it, is very limited and counts just one tenth of that of palladium. Therefore, it seems wise to separate palladium selectively and let *ruthenium and rhodium to be disposed with the vitrified waste. The present thesis is a fundamental study on preparation and* characterization of the stable alginate microcapsule for the selective uptake of palladium and two other soft metal ions (*i.e.* Ag and Cd) from HLLW. Separation of silver and cadmium is important due to their interference in separation-purification of palladium. Moreover this work has aimed a fundamental rather than a practical study; thus for it, it is important to check uptake mechanisms in different acidity and concentrations. Unfortunately high concentration of palladium precipitates at higher pHs, thus for clarification of essential mechanisms cadmium and especially silver are preferred.

Alginate microcapsules (hereinafter MCs) have a number of advantages for separation of above-mentioned soft metal ions, including simplicity of preparation procedure, high selectivity toward soft metal ions due to the enclosed Cyanex 302 extractant, and acid resistance.

The premium (hereinafter uncoated) alginate MCs were prepared as follows: Cyanex 302 extractant (1.2 g) was fully dispersed in 100 cm^3 of 2.4 % sodium alginate solution. The kneaded sol was injected into 0.1 M Ca $(NO_3)_2$ solutions, stirred for 6 hr, and then the formed MCs were separated, and finally dried at 40°C. MCs after drying have an average size of 605 μm, with a uniform dispersion of extractant microdroplets in its matrix (Figure 1).

Uncoated alginate MCs despite of having a simple preparation procedure, suffer from the leakage of extractant (HA), so that after 100 h contact with 0.1 M HNO_3, in the packed column , they loss about 5% of their initial extractant content. Acid concentration however has a very slight effect on the leakage rate, so that the maximum leakage which occurs at 0.5 M HNO_3 is only 1% and



(a) (b)

Figure 1. (a) Typical morphological and (b) cross sectional SEM images of MCs.

2 % more than those in 0.1 M HNO_3 and pure water, respectively.

Lakage problem can be solved by either coating of MCs or by modification of their matrices. Coating itself could be by water soluble polymers such as chitosan or polyethyleneimine (PEI) which due to having the cationic functional groups (NH^+ or NH_2^+) crosslink with alginate polymers with the opposite charge, or by thermoset polymers such as urea formaldehyde. For matrix modification an ammoniacal solution of cellulose acetate phthalate (CAP) was added to sodium alginate solution immediately before dispersion of HA.

The stability tests have revealed that 1. Coating by chitosan causes of losses of extractant during the coating 2. Coating by PEI, leads to an impermeable MC, nevertheless it to an extent suppress the kinetics of uptake and reduce the column performance 3. Coating by urea formaldehyde often leaves some unreacted formaldehyde in the MCs that during uptake reduces ions such as Ag^+ to their metallic form. 4. Matrix modification is not only free from above-mentioned drawbacks of coating, but also increase the absorption capacity and column performance of MCs, probably due to the absorption ability of CAP polymer.

Both matrix and extractant of alginate MCs have adsorption ability, with much higher affinity of the later toward the soft metal ions. The equilibrium uptake experiments showed that until nearly all HA molecules have not been saturated with the soft

metal ions, the alginate matrix may not participate in the adsorption. If concentration of soft metals is under a definite limits (hereinafter breakpoint) uptake takes place via solvent extraction mechanism. Above breakpoint matrix adsorbs the target ions by ion exchange.

While the uptake by extractant is not affected by existence of coexisting ions such as H^+, Na^+ or Ca^{2+}, adsorption by alginate matrix is significantly affected. Thus, at higher concentration of coexisting ions uptake capacity of MCs approaches to the capacity of only extractant. At elevated acid concentration, extractant also losses its uptake ability; but the acid concentrations beyond which declining of uptake ability of extractant becomes significant has following order depending on the type of soft metal ions

$$Cd^{2+}\ (0.3\ M\ HNO_3) < Ag^{+}\ (1\ M\ HNO_3) < Pd^{2+}\ (3\ M\ HNO_3)$$

The kinetics mechanism and the rate determining step were found to vary depending on the concentration of coexisting ions. In the presence of low concentration of coexisting ions, kinetics is controlled by a slow chemical reaction of HA microdroplets and soft ions. Reaction controlled shrinking core model as follow found to be an appropriate mathematical model for this case.

$$1-(1-X)^{1/3} = \frac{k''}{\rho R}\int_0^t Cdt \qquad (1)$$

In the presence of even moderate concentrations of coexisting ions, alginate significantly loses its uptake ability, thus it can not act as ion carrier for HA. In this case, ions are transferred to HA micro droplets merely via the water trapped in pore of MCs. Consequently kinetics becomes very slow and rate determining step changes from chemical controlled to intra-pore diffusion control. Since chemical reactions between HA and target ions is much faster than rate of diffusion, and also due to high affinity of HA toward soft metal ions, all of soft ions that reach to reacting layer are adsorbed by it and can not reach to the unreacted core. The outer layers have been already spent off. This "shielding effect", further decelerate the rate of uptake because at any given time of "t" only a thin reacting layers is adsorbing the ions. The overall picture of reaction quite fits with following intra-particle diffusion control shrinking core model

$$1-3(1-X)^{2/3}+2(1-X) = \frac{6D_e}{C^0R^2}\int_0^t Cdt \qquad (2)$$

In column operations, at low concentration of coexisting ions (*e.g.* $[H^+] \leq 0.001M$), total uptake capacity of MCs (about 1.2 meq/g), is given by superposition of capacity of matrix and extractant. In most of practical cases, where concentration of coexisting ions (*e.g.* $[H^+] > 0.01M$), is over medium, total capacity of MCs approaches to the capacity of only extractant (0.76 meq/g)

Table 1. Effect of operational parameters on performance, $[Pd^{2+}]$ =100 ppm, $[H^+]$=0.12M.

Ion	Adsorbent	Mass (g)	Flow rate (cm^3/min)	Diameter (mm)	Residence time (min)	Breakthrough volume (cm^3)	Utilization factor (%)
Pd^{2+}	***MC-1***	0.5	0.25	8	5.22	19	9.5
Pd^{2+}	***MC-1***	0.5	0.25	5	5.22	32	14.7
Pd^{2+}	***MC-1***	1	0.5	8	5.22	58	12.2
Pd^{2+}	***MC-1***	1	0.5	5	5.22	105	21.5
Pd^{2+}	***MC-1***	1	0.25	8	10.44	200	38.8
Pd^{2+}	***MC-1***	1	0.25	5	10.44	265	52.2

independent of type of coexisting ions (asymptotic behavior). Enhancement of the asymptotic total capacity by increasing the weight percentage of extractant although is possible but leads to the increasing size of MCs and consequently deterioration of kinetics and practical capacity (*i.e.* capacity up to breakthrough point).

The selectivity of alginate MCs is amid of those of chelating resins and strongly acidic ion–exchangers (Figure 2). Chelating resins are highly selective, and coexisting ions nearly have no effect on their breakthrough behavior. Strongly acidic ion exchangers on the other hand loss both of their total capacity and performance in presence of coexisting ions. Behavior of alginate MCs at 0.001 M H^+ is quite different with that at 0.01 M H^+, but due to asymptotic behavior, there is only a slight difference between behavior at $[H^+]$ = 0.01 M and $[H^+]$ = 0.1 M.

For alginate MCs, likewise to chelating resin, intraparticle resistance control the kinetics, thus column performance is very sensitive to variation of operational parameters. Table (1) shows that the most important factor affecting on the column performance is the residence time. At the same residence time, larger mass is preferred because the column capacity becomes larger. Diameter of column, when mass and residence time are fixed, has minor effect on performance.

Alginate MCs show a high selectivity toward Pd^{2+} over $RuNO^{3+}$ and Rh^{3+} which are the dominant species of ruthenium and rhodium in HLLW. Figure 3 shows ruthenium and rhodium pass the MCs column nearly with no adsorption. Palladium is selectively adsorbed, but it has a well shaped breakthrough curve (with large breakthrough volume) only when the mass of MCs is sufficiently large (about 1 g). With 1.5 g MCs, palladium was separated in the presence of 1 M HNO_3 + 0.92 M Na^+. Probably, final goal of the study that is selective uptake of palladium from HLLW containing 2.5 M HNO_3 +0.92 M Na^+ by employing larger mass of MCs will be achievable, because as was previously mentioned alginate MCs are able to take up 99% of Pd^{2+} from a solution containing 3 M HNO_3. In Figure (3) loading ratio of Ru and Rh in comparison to palladium was Pd/ Rh/ Ru =1/ 0.014/ 0.025. These ratios were obtained by destructive dissolution of MCs in nitric acid 60% by 10 h heating at 160°C in a Teflon bomb, followed by analyses of Pd, Rh and Ru by ICP-AES.

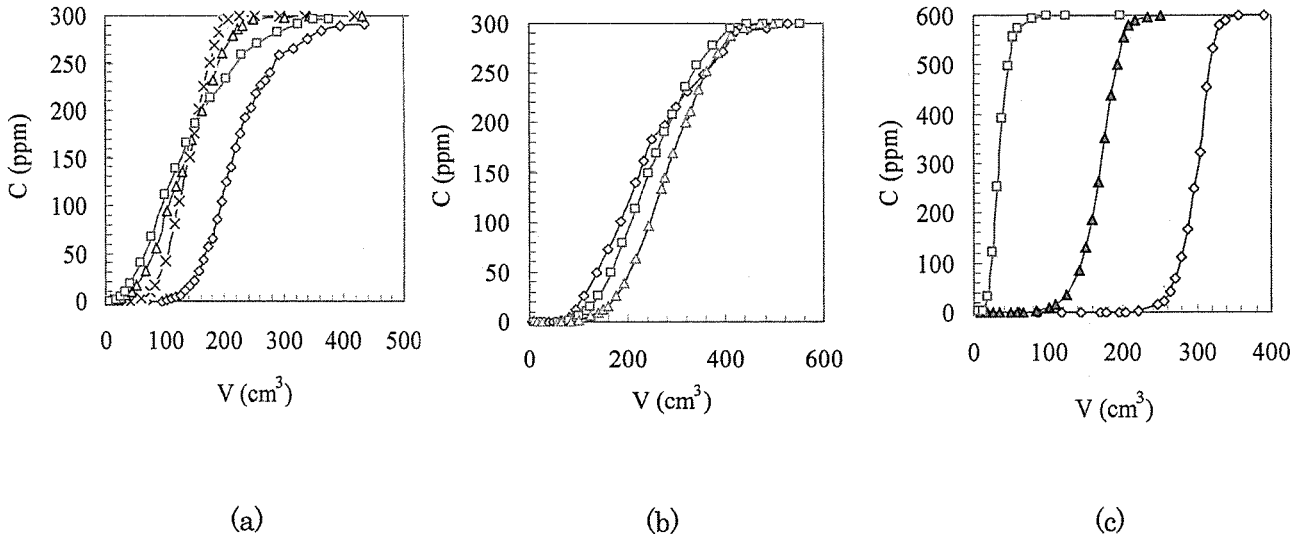


Figure 2. Effect of coexisting ions on breakthrough behaviors in Ag^+ adsorption by (a) alginate MCs, (b) Lewatite TP 214 chelating resin, (c) Amberlite 200 CT strongly acidic ion exchangers; in all charts: ◊ 0.001 M H^+, □ 0.01 M H^+, Δ 0.1 M H^+, + 0.1M Ca^{2+}.

A simplified analytical model for prediction of breakthrough behavior of chelating and alginate MCs was developed on the bases of shrinking core model (SCM) and constant pattern approximation (CPA). Model has the following mathematical form

$$V - V_b = A\,Ln\left(\frac{X}{X_b}\right) + B\left[F(X) - F(X_b)\right] \tag{3}$$

where $F(X)$ is defined as

$$F(X) = \left[\left(\frac{1-(1-X)^{1/3}}{X}\right) + \frac{2}{\sqrt{3}}\,arctg\left(\frac{2(1-X)^{1/3}+1}{\sqrt{3}}\right)\right] \tag{4}$$

In equations (3) and (4) V and X show volume and dimensionless concentration ($X=C/C_0$), C_0 denotes initial concentration, A and B are two adjustable parameters, and index b shows conditions at breakthrough point where X=0.01.

In addition to equation (3) and (4), calculations need two experimental correlations, that are a linear relation between C_0 (V_e-V_b) and Q-C_0V_b where Q is total capacity of column (mmol) and V_e shows the exhaustion volume (V at X=0.925), and another linear correlation between operational group $q_{sat}\,v\,/C_0$) and the adjustable parameter B, where q_{sat} and v denotes adsorption capacity

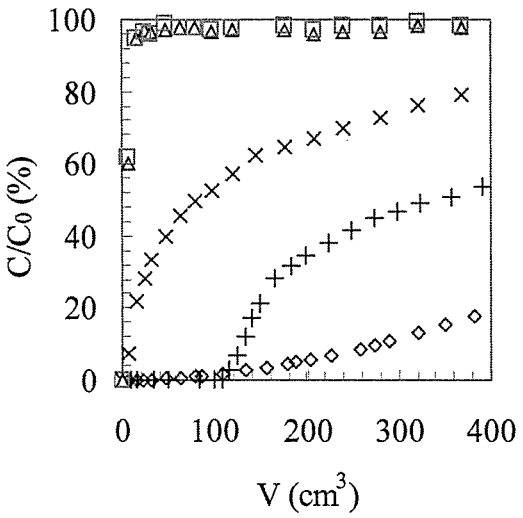


Figure 3. (a) Separation of Pd^{2+} from a solution of 100 ppm Pd^{2+}, 36 ppm Rh^{3+} and 100 ppm $RuNO^{3+}$; □ Rh^{3+}, ▲ $Ru(NO)^{3+}$, × (Pd^{2+} , $[H^+]$=1 M), × (Pd^{2+} , 0.5g, $[H^+]$=1 M), ◊ (Pd^{2+} , 1 g, $[H^+]$=1 M), + (Pd^{2+} , 1.5g, $[H^+]$=1 M, $[Na^+]$=0.92 M).

of adsorbent (mmol/g) and flow rate (cm^3/min), repectively.

As for obtaining two above-mentioned correlations a few experimental data should be used in a trial and error process along with the following equation.

$$Q = C_0(V_b + 3.615A + 0.238B) \tag{5}$$

As for finding three parameters A, B and V_b for an unknown case under design, it is enough to use these two above-mentioned correlations along with equation of (5). The model could successfully estimate the breakthrough and exhaustion points for adsorption of Ag^+ ions by Lewatite TP-214 chelating resin, and fit the experimental curves (Figure 4). In the case of alginate MCs, although model can fit the experiments with less than 3% error, but dependency of B to operational group ($q_{sat}\,v\,/C_0$) is not linear and still needs further studies.

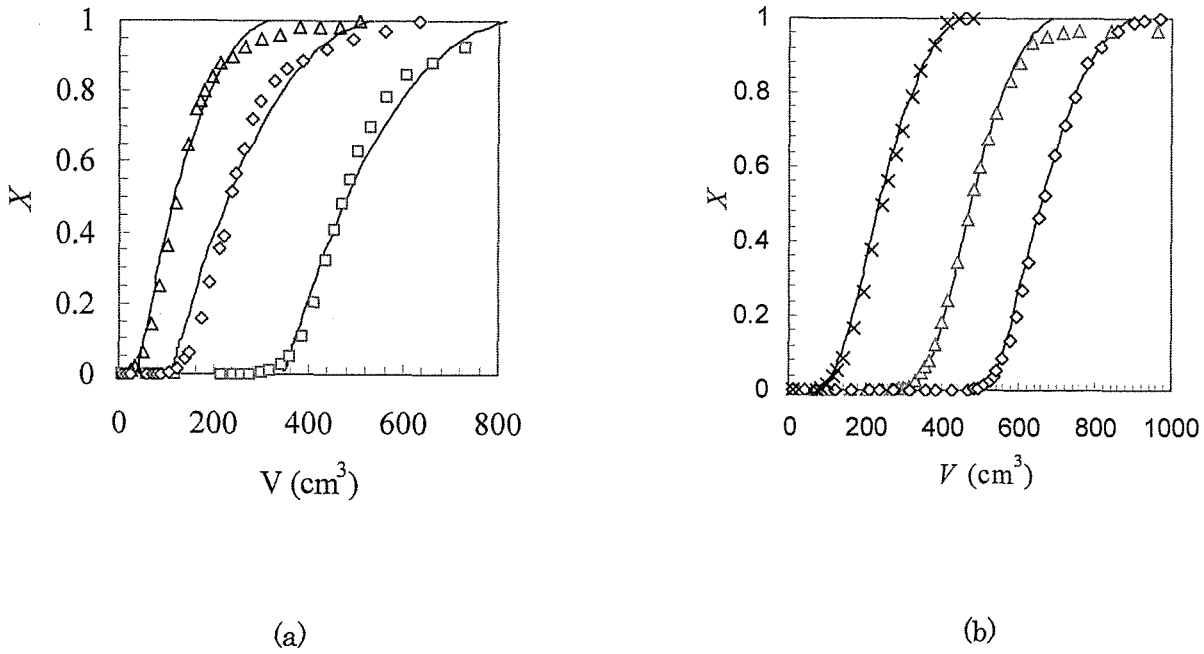


Figure 4. Comparison of model and experiments, (a) for MCs at 0.001 M H^+, All about 600 ppm Ag^+ and 0.5 cm^3/min; Δ 0.5 g, ◊ 1 g, □ 2 g, (b) for Lewatite TP 214 chelating resins at 0.01M H^+; × exp. 0.5 cm^3/min, 0.4g,300 ppm, , Δ exp. 0.48 cm^3/min, 0.8g, 300 ppm, ◊ exp. 1cm^3/min, 2 g, 593 ppm, In all cases solid lines show calculated curve.

論文審査結果の要旨

原子力などの大規模なエネルギーの利用は人類にとって重要な技術であるが、放射性物質の生成を伴うため環境の保全をあわせて必要とする。放射性物質を選択的に分離・回収する高機能性材料を開発し、資源の有効利用や環境負荷低減化に寄与する研究は、先進的な核燃料サイクルを実現するための重要な課題である。特に、再処理工程から発生する高レベル放射性廃液（HLLW）中に含有されるソフトメタル（Pd, Ag, Cd 等）は、その分離技術が未完成であり、選択的に分離回収できる新規な機能性分離吸着剤の創成および吸着特性の評価が期待されている。さらに、高レベル廃液中のソフトメタルの選択的分離回収は、廃棄物処分への負担低減化および核種の有効利用の両面での効果が期待できる。以上の観点から、機能性分離吸着剤として核種選択性を有する S ドナー含有抽出剤を選択し、本分離剤を安定に包括固定化できるマイクロカプセル化手法を新たに構築することにより、ソフトメタルの選択的分離回収の可能性を基礎的に検討した。

本研究では，新規なマイクロカプセル化手法の検討、キャラクタリゼーションおよび安定性評価試験を実施すると共に、酸性度、共存イオン濃度、温度をパラメーターとして吸着特性（分配特性、吸着速度）を評価した。またカラム設計に適用するための吸着反応モデルを明らかにし、他吸着剤との比較検討およびその適用性を基礎的に評価した。本論文は、その研究成果をまとめたもので全編 6 章よりなる。

第 1 章は序論であり，本研究の背景と目的を述べている。

第 2 章では，新規マイクロカプセルの調製と本マイクロカプセルの安定化技術（多重被覆法およびマトリックス修飾法）の開発を実施した。調製したマイクロカプセルのキャラクタリゼーション（表面形態、被覆厚、抽出剤の溶出、化学的安定性、抽出剤含有率、吸着容量および耐熱性）を行うことにより、各マイクロカプセルの安定性評価を行ないマトリックス修飾マイクロカプセルの有効性を明らかにした。

第 3 章では，マイクロカプセルへのソフトメタルの吸着平衡および吸着速度について検討した。吸着平衡および吸着速度は、酸性度、共存イオン濃度および反応温度等をパラメーターとして評価した。金属イオンの初期制限濃度（breakpoint）以下では抽出剤への溶媒抽出反応、それ以上ではアルギネートマトリックスへのイオン交換反応が支配的であることを明らかにし、3 M Na^{+}イオン共存下でも 90 %以上の吸着率を示すことを実証した。また、収縮核モデル（shrinking core model）により吸着反応の実験結果を解析可能であることを見出した。

第 4 章では、ソフトメタルのカラム吸着特性を、パラメーターとして流速、充填カラム長さ、共存イオン濃度、担持量等を変化させて検討した。特に、マトリックス修飾マイクロカプセルによるカラム特性は被覆マイクロカプセルに比べて優れていること、1 M 硝酸ナトリウムと 1 M 硝酸の混合溶液から Pd^{2+}イオンを選択的に吸着できること、Rh^{3+}イオンおよび $Ru(NO)^{3+}$イオンとの分離性が良好であること、効率的な溶離が可能であること等を明らかにした。

第 5 章では、マイクロカプセル充填カラムとキレート樹脂充填カラムにおける破過特性を、通液条件を変化させ比較検討すると共に、収縮核モデルを用いて破過特性のモデル解析を行った。破過データは収縮核モデルと整合性が認められ、その誤差は 3%以内であることを実証した。本モデルを用いることにより、選択的かつ効率的なソフトメタル吸着分離に応用可能であり、実用的なカラム設計に有効であることを明らかにした。

第 6 章では，本研究で得られた成果について要約している。

以上，本論文では，高機能性マイクロカプセルを合成し、そのキャラクタリゼーションおよび安定性評価を行い、高レベル廃液からのソフトメタル（Pd, Ag, Cd 等）の選択的な吸着特性（分配特性、反応速度）を明らかにした。また、カラム設計に有効な吸着モデルを提案し、破過データとの整合性が良好であることを実証した。本研究は、先進的な核燃料サイクルにおける廃棄物処理での核種精密分離への応用・展開が可能であることを示したもので、量子エネルギー工学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。